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（合成ガスから効率的なアルコール製造用ナノ触媒の設計）

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学位論文内容の要旨

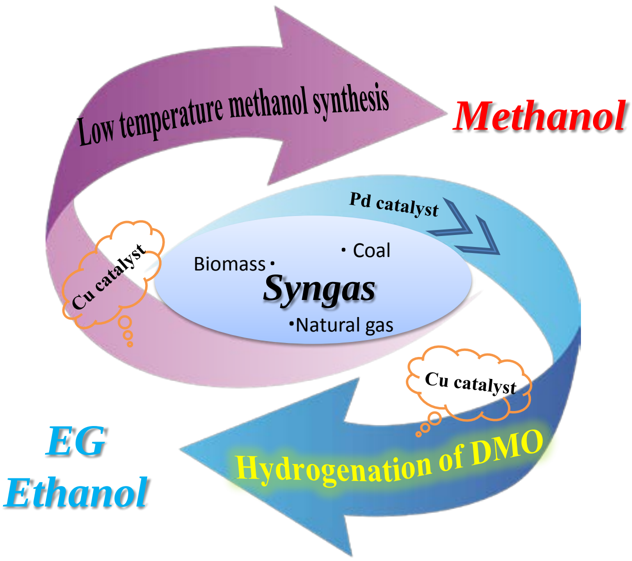
学位論文題目　Designing nano catalysts to realize effective alcohols production from syngas
（合成ガスから効率的なアルコール製造用ナノ触媒の設計）

ナノ新機能物質科学専攻

氏名　艾培培（Peipei Ai）

With increasing attention to the energy crisis and environmental issues, more and more researchers focus on catalytic methods for the efficient and clean utilization of abundant coal and biomass resources, causing a rapid global development of C1 chemistry. C1 chemistry refers to the conversion of simple carbon-containing materials that contain one carbon atom per molecule into valuable products. As one of important feedstocks for C1 chemistry, syngas (a mixture of carbon monoxide and hydrogen), which is primarily produced from coal, natural gas or biomass, has attracted great attention in recent years. From syngas, high-quality liquid products can be produced via gas-to-liquids technology. Notably, efficient production of high value-added alcohols from syngas has been intensively explored owing to its academic and industrial value.

Alcohols are compounds in which one or more hydrogen atoms in an alkane have been replaced by an -OH group. Alcohols are a kind of extremely important products, which can used as synthetic intermediate, cleanser, cosmetics, fuel, alcoholic beverages, etc. As an important class of alcohols, methanol, ethylene glycol (EG) and ethanol can be manufactured from syngas conversion via the following route: methanol via low-temperature methanol synthesis; EG as well as ethanol via the hydrogenation of dimethyl oxalate (DMO). The production of methanol via low-temperature methanol synthesis route from CO_2-containing syngas is proposed and developed by our lab. In this route, the added alcohols act as homogeneous co-catalysts and the solvent, realizing high one-pass conversion at only 5.0 MPa and 170 ^oC. This new route changes the normal reaction path of conventional, high-temperature methanol synthesis from formate via methoxy to methanol. Ethanol, as well as EG, are attractive products and important chemical raw material for the synthesis of various products (e.g., chemicals, fuels and polymers), which are mainly produced from petroleum-derived ethylene in the present industrial approach. On account of the diminishing fossil-fuel resources, developing an alternative synthesis method for EG and ethanol from syngas has attracted increasing attention. As one of the promising applications to C1 chemistry, the hydrogenation of DMO to EG and ethanol draw much attention since the mass production of DMO was commercially realized by the synthesis method via syngas.



Although considerable efforts have devoted in the study of above-mentioned reactions, the development of nano catalyst for efficient alcohols production from syngas is still challenging and promising from commercial application prospect.

In chapter 1, a novel method is developed to prepare nano catalyst (Cu-ZnO/RHA) directly without further reduction for low-temperature methanol synthesis. In this method, the low-valued by-product rice husk (RH) is not only used as the catalyst support precursor, but also as the reductant and fuel. The as-burnt Cu-ZnO/RHA is directly applied in low-temperature methanol synthesis from $CO/CO_2/H_2$ using ethanol as a catalyst and solvent. The activity of the as-burnt catalyst prepared by this novel method without further reduction is much higher than that prepared by a conventional impregnation method which is already after 10 h reduction at 250 ^{o}C by 5% H_2.

In chapter 2, an auto-reduced nano catalyst with copper (Cu) nanoparticles encapsulated inside the nano-channels of carbon nanotubes (CNTs) is designed and prepared for the selective hydrogenation of DMO. Due to the interaction of Cu species with electron deficient interior surface of CNTs, calcination process of catalysts can directly realize the auto-reduction of Cu oxide with CNTs itself as reductant. Furthermore, the auto-reduction degree of Cu@CNTs catalyst can be facilely tuned by changing the calcination temperature. In dimethyl oxalate (DMO) hydrogenation reaction, the auto-reduced Cu@CNTs catalyst without pre-reduction exhibits excellent catalytic activity, high target product selectivity and catalytic efficiency.

In chapter 3, a series of boron-doped carbon nanotubes supported Cu catalysts (Cu/xB-CNTs) are designed and prepared by thermal treating CNTs in the presence of boric acid followed by post impregnation with Cu species, and their catalytic performances are comprehensively evaluated in the hydrogenation of DMO to ethanol. The structure and chemical properties of boron-doped catalysts are well characterized by means of various techniques, giving strong evidences for structure and performance modifications due to the boron doping. Significant improvements in catalytic activity and stability can be achieved by boron-doped Cu/xB-CNTs catalysts.

By means of above work, a series of problems in alcohols production from syngas are well solved in this thesis. Novel nano catalysts for efficient alcohols production from syngas were successfully designed and prepared in this thesis. The catalytic efficiency and selectivity of expected products are greatly enhanced with these new fabrication and design of catalysts.

【論文審査の結果の要旨】(Peipei Ai)

当学位審査委員会は本論文を詳細に査読・審査し、かつ論文審査会を平成29年8月10日公開で開催し、その発表と質疑応答について審査した。その審査結果を要約する。

本論文は合成ガス（一酸化炭素と水素の混合ガス）からのメタノール合成、および新規エタノール合成に関する研究である。本論文は四章で構成される。各章の要約を以下に示す。

第一章では新規低温メタノール合成について、応用される銅—酸化亜鉛触媒の新規調製方法として、稲わらを用いた自己燃焼法を開発し。新規調製法で得られた触媒が高い活性を示した。更に各種の物理・化学分光手法を用いて新規触媒調製法のメカニズム、並びに触媒反応のメカニズムを解明した。

第二章はシュウ酸ジメチル(DMO)からエタノールの新規合成方法と新規触媒の開発である。宇部興産（株）はPd触媒とNO触媒の混用によって、合成ガスからDMOの合成に成功し、更にDMOの水素化によってエチレングリコール(EG)の工業化生産を全世界の産炭国で操業している。本研究はDMOの水素化によってエタノールの生産を試みた。カーボン・ナノ・チューブ(CNT)胴体内部に搭載された銅ナノ粒子触媒をイナート雰囲気で高温焼成・還元処理を施した状態は非常に高いエタノール合成能力を有することを発見した。各種触媒調製条件、触媒反応条件を最適化し、各種分光計測法を用いて触媒合成の連続反応メカニズムを明らかにした。CNT内部電子空間分布と銅カチオン、金属銅のナノ粒子間の電子授与強度は反応生成物分布を支配していることも分かった。

第三章はDMOの水素化によるエタノール合成触媒の改善である。カーボン・ナノ・チューブ(CNT)胴体内部に搭載された銅ナノ粒子触媒に関して、銅ナノ粒子とCNT内表面の相互作用をチューニングすれば、銅触媒とCNT内部電子間の電子授与強度を制御でき、触媒反応生成物分布もコントロールできる。ホウ素ドーピングしたCNTを調製し、胴体内部に搭載された銅ナノ粒子触媒を調製し、より高いエタノール合成活性を収めた。各種分光計測法を用いて触媒反応機構を解析した結果、+３価のホウ素と+４価の炭素間新たに生まれた弱いLewis酸点は+１価の銅触媒サイトの生成と維持に貢献し、律速段階の反応速度を加速したと判明した。

第四章は、上記第一章から第三章までのまとめである。

上記の内容は国際学術専門誌に原著論文３報（関連論文３報）として掲載された。

当審査委員会は以上を総合的に判断した結果、審査論文は、エネルギー、環境、無機化学合成、触媒化学諸分野において、学術的価値のある知見を与え

ていると判断し、博士の学位論文として十分な価値を有し、博士の学位を授与するに値する論文であると判定した。